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(54) Surface reflecting mirror with three protective layers

(57) A high-reflectivity surface reflecting mirror 101 is provided by sequentially forming, on a resin substrate 102, a silicon dioxide under layer 103, an aluminium reflecting layer 104, a silicon dioxide first protective layer 105, a second protective layer 106 made of at least one of titanium oxide, tantalum oxide and zirconium oxide, and an aluminum oxide third protective layer 107.

FIG. 2

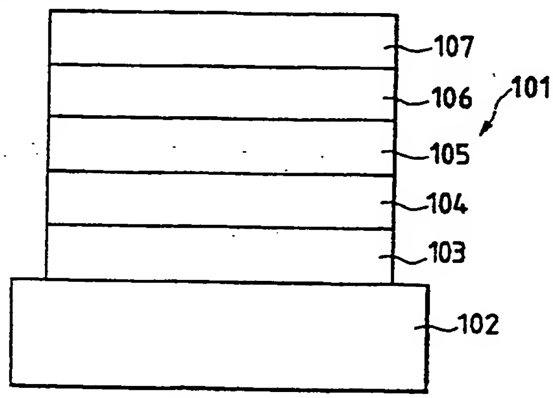

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FIG. 1

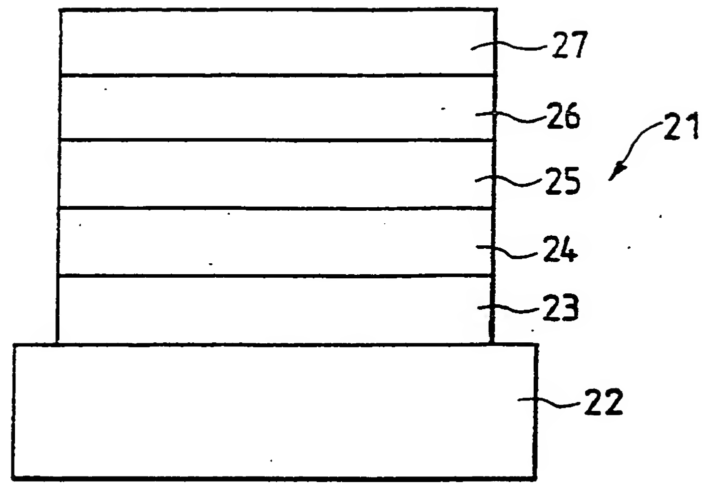


FIG. 2

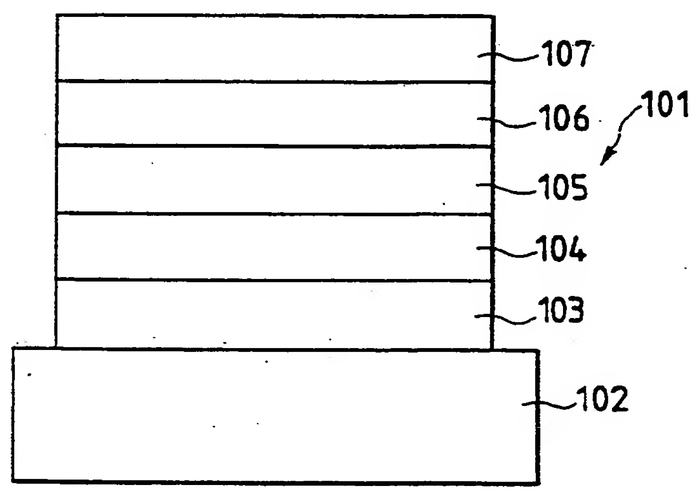


FIG. 3

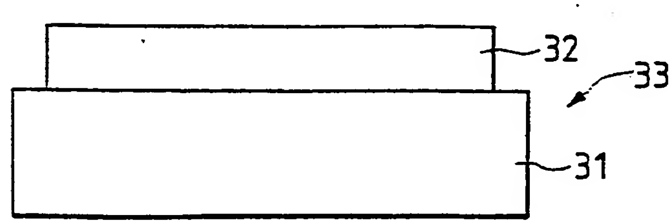


FIG. 4

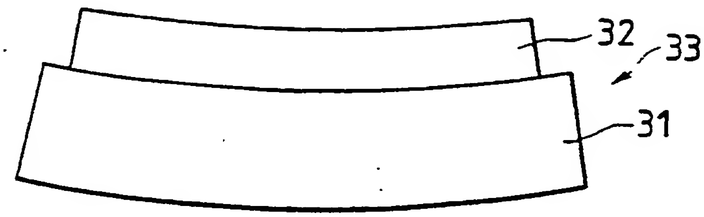


FIG. 5

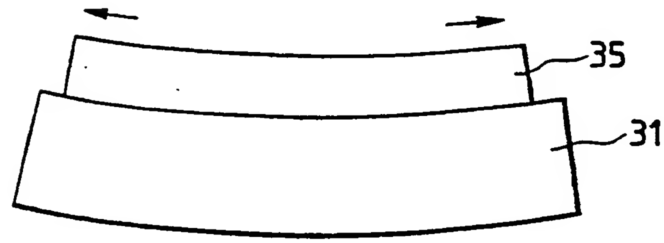


FIG. 6

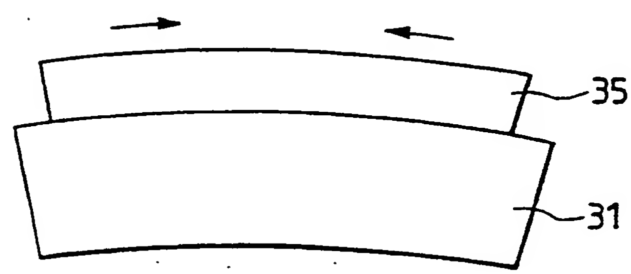
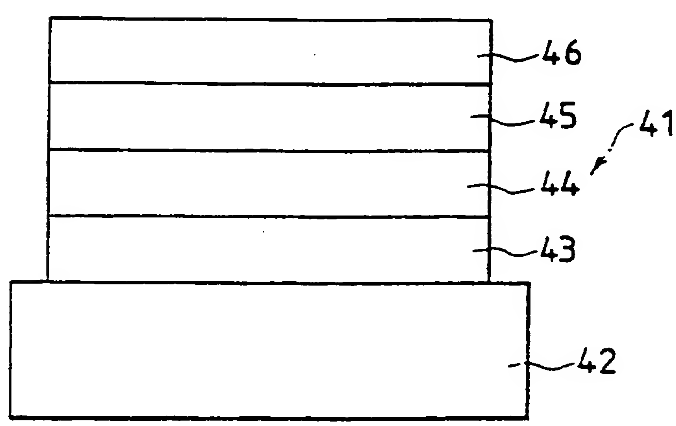


FIG. 7



SURFACE REFLECTING MIRROR

The present invention relates to a surface reflecting mirror having a surface reflecting multilayer film that is used in optical products such as cameras, telescopes and microscopes.

In a surface reflecting mirror used in optical products such as cameras, telescopes and microscopes, aluminum is most commonly used as a reflecting material. However, sufficient resistance to scratching, resistance to humidification, etc. cannot be obtained simply by forming an aluminium reflecting layer on a substrate. Conventionally, this problem has been solved by forming a protective layer of an oxide of silicon, magnesium fluoride, etc.

Silver, which has a high reflectivity over a visible to near infrared range, is commonly used as a reflecting material for a high-reflectivity surface reflecting mirror that is used in optical products. However, a single layer film of silver is inferior in film adhesiveness, resistance to humidification, resistance to sulfurizing, etc. In order to improve these characteristics, a multilayer film is formed by the silver single layer film, an under layer and protective layers.

The durability of this type of high-reflectivity surface reflecting mirror is evaluated by an accelerated test for resistance to humidification at 40-60°C. When the above high-reflectivity surface reflecting mirror was subjected to a test for resistance to humidification at 60°C and 90% RH for 24 hours, it was sometimes the case that the laminate films peeled off from the substrate to cause point-like defects. It is considered that the point-like defects are caused by the thermal expansion or the swelling by damping of the resin.

Although the point-like defects gradually disappear if the reflecting mirror is again placed in a usual atmosphere, they will deteriorate the film adhesiveness to thereby lower the durability of the reflecting film 2c.

In recent years, due to the development of ultra-high-precision die-machining tools and the improvements of the injection molding technique, resins have come to be used as optical members. In particular, engineering plastics such as a polycarbonate resin and a polyacetal resin are superior in durability, and can be used at a high temperature. However, even with the engineering plastics the problems originating from the occurrence of the point-like defects have not been solved yet.

An object of the invention is to provide a surface reflecting mirror in which no point-like defects occur between a resin substrate and a reflecting film structure even in a high temperature, high humidity atmosphere.

According to the invention there is provided a surface reflecting mirror comprising:

a resin substrate;

an under layer made of silicon dioxide and formed on the resin substrate;

a reflecting layer made of aluminium and formed on the under layer;

a first protective layer made of silicon dioxide and formed on the reflecting layer;

a second protective layer made of at least one material selected from the group consisting of titanium oxide, tantalum oxide and zirconium oxide, and formed on the first protective layer; and

a third protective layer made of aluminum oxide and formed on the second protective layer.

The silicon dioxide under layer imposes a compressive stress on the resin substrate, and its thickness can be changed without influencing the optical characteristics of the surface reflecting mirror. By adjusting the thickness of the under layer without needing to consider the optical

characteristics, the tensile stress imposed by the entire reflecting film structure on the substrate can be reduced or changed to a compressive stress. As a result, a surface reflecting mirror can be provided which is hardly bent, and in which no point-like defects occur between the resin substrate and the reflecting film structure, by virtue of a reduced influence of the expansion of the substrate even in a high temperature, high humidity atmosphere.

The invention will further be described, by way of example, with reference to the accompanying drawings, in which:

Fig. 1 is a side view of a conventional surface reflecting mirror;

Fig. 2 is a side view of a surface reflecting mirror according to an embodiment of the invention;

Fig. 3 is a side view of a surface reflecting mirror under a normal condition;

Fig. 4 is a side view showing how a surface reflecting mirror is bent in a high temperature, high humidity atmosphere;

Fig. 5 is a side view illustrating a tensile stress in a surface reflecting mirror;

Fig. 6 is a side view illustrating a compressive stress in a surface reflecting mirror; and

Fig. 7 is a side view of surface reflecting mirrors of reference examples 3-5.

In studying the causes of the point-like detects, the present inventor has found the following phenomenon.

When, for example, a surface reflecting mirror 33 having a resin substrate 31 and a reflecting film structure 32 formed thereon (see Fig. 3) is placed in a high temperature, high humidity atmosphere, the reflecting film structure 32 expands only slightly in contrast to a large thermal expansion or damping expansion of the resin substrate 31. Therefore, as shown in Fig. 4, the surface reflecting mirror 33 bends to assume a shape concave to the side of the reflecting film structure 32. This bending due to the expansion of the substrate 31 is the main cause of the point-like defects.

Further, if a unit layer 35 of reflecting films, protective films, or the like is formed on the resin substrate 31, a tensile stress or compressive stress remains in the unit film 35 as shown in Figs. 5 and 6.

The residual tensile stress tends to bend the surface reflecting mirror 33 so that it assumes a shape concave to the side of the unit film 35, as shown in Fig. 5. On the other hand, the residual compressive stress tends to bend the surface reflecting mirror 33 so that it assumes a shape concave to the side of the substrate 31, as shown in Fig. 6.

Measurements of a surface shape variation before and after the formation of a unit film on the substrate

have revealed that in the case of the surface reflecting mirror 21 as shown in Fig. 1, among the films 23-27 formed on the resin substrate 22, the tensile stress remains in the under layer 23 made of chromium oxide, the reflecting layer 24 made of aluminium, the second protective layer 26 made of titanium oxide, tantalum oxide or zirconium oxide and the third protective layer 27 made of aluminium oxide while the compressive stress remains in the first protective layer made of silicon dioxide. That is, in the surface reflecting mirror 21, the entire reflecting film structure imposes the tensile stress on the resin substrate 22. Therefore, when the surface reflecting mirror 21 is placed in a high temperature, high humidity atmosphere, it is easily bent so as to assume a shape concave to the side of the reflecting film structure due to the thermal expansion or damping expansion of the substrate 22.

Fig. 1 shows a surface reflecting mirror having a five-layer reflecting film structure. As shown in the figure, a surface reflecting mirror 21 is formed by sequentially laying, on a resin substrate 22, a chromium oxide under layer 23, an aluminium reflecting layer 24, a silicon dioxide first protective layer 25,

a titanium oxide second protective layer 26 and an aluminium oxide third protective layer 27.

In this film structure, adhesion of the aluminium reflecting layer 24 to the resin substrate 22 is improved, so that the film structure does not peel off in the tape test.

However, even the above surface reflecting mirror 21 has the following problem. That is, when the surface reflecting mirror 21 is placed in a high temperature, high humidity atmosphere at 60°C and 90% RH for a long period, point-like defects (local peeling off the film structure from the resin substrate 22) occur due to the thermal expansion or damping expansion of the resin. Although the point-like defects gradually disappear when the surface reflecting mirror 21 is again placed in a usual atmosphere, they may deteriorate the adhesiveness of the reflecting film structure to the resin substrate 22.

Fig. 2 is a side view showing a surface reflecting mirror according to an embodiment of the invention. As shown in the figure, a surface reflecting mirror 101 is formed by sequentially laying, on a resin substrate 102, an under layer 103, a reflecting layer 104, a first protective layer

105, a second protective layer 106 and a third protective layer 107.

The substrate 102 of the surface reflecting mirror 101 is made of a resin material without any specific limitations thereon. The resin material may be a polycarbonate resin, polyacetal resin, acrylic resin, polystyrene resin, polyimide resin, polyethylene terephthalate resin, plybutylene terephthalate resin, ABS resin, or the like.

The under layer 103 made of silicon dioxide serves not only to improve the adhesiveness of the reflecting layer 104 to the resin substrate 102 but to lessen, by the compressive stress occurring when the under layer 13 is formed, the influence of the thermal expansion or damping expansion of the resin substrate 102. The thickness of the under layer 103 is properly determined in accordance with a force of bending the surface reflecting mirror 101 that originates from the thermal expansion coefficient and damping expansion coefficient of the selected resin substrate 102, the tensile stress imposed by the reflecting layer 104 and the protective layers 105-107 on the substrate 102 and other factors. The thickness of the under layer 103 is usually within the range of 50-350 nm, and preferably within the range of 50-300 nm.

The reflecting layer 104 is made of aluminum, and has a thickness usually within the range of 50-250 nm, and preferably within the range of 100-200 nm. The thickness

smaller than 50 nm is not appropriate because in such a case the surface reflecting mirror 101 becomes like a half mirror.

The first protective layer 105 is made of silicon dioxide, and serves as a low refractive index layer for enhancing the reflection in the visible range. The thickness of the first protective layer 105 is usually within the range of 42-133 nm, and preferably within the range of 70-105 nm.

The second protective layer 106 is made of at least one material selected from titanium oxide, tantalum oxide and zirconium oxide, and serves as a high refractive index material for enhancing the reflection in the visible range. The thickness of the second protective layer 106 is usually within the range of 24-89 nm, and preferably within the range of 45-70 nm.

The third protective layer 107 is made of aluminum oxide, and serves to protect the second protective layer 106 which is deficient in durability. The thickness of the third protective film is usually within the range of 10-110 nm, and preferably within the range of 10-80 nm. If the thickness is smaller than 10 nm, sufficient durability is not obtained. If the thickness exceeds 110 nm, the third protective layer 107 reduces the reflection enhancement effect created by the combination of the first and second protective layers 105 and 106.

Examples 1-3

A surface reflecting mirror 101 as shown in Fig. 2 was manufactured by forming the following layers on a polycarbonate resin substrate 102 of 2 mm in thickness by vacuum evaporation: a silicon dioxide under layer 103 having a thickness of 50 nm (example 1), 200 nm (example 2) or 350 nm (example 3), an aluminium reflecting layer 104 of 100 nm in thickness, a silicon dioxide first protective layer 105 of 52 nm in thickness, a titanium oxide second protective layer 106 of 33 nm in thickness, and an aluminium oxide protective layer 107 of 45 nm in thickness.

<u>Examples 4-6</u>

A surface reflecting mirror 101 as shown in Fig. 2 was manufactured by forming the following layers on a polycarbonate resin substrate 102 of 2 mm in thickness by vacuum evaporation: a silicon dioxide under layer 103 having a thickness of 50 nm (example 4), 200 nm (example 5) or 350 nm (example 6), an aluminium reflecting layer 104 of 100 nm in thickness, a silicon dioxide first protective layer 105 of 52 nm in thickness, a tantalum oxide second protective layer 106 of 36 nm in thickness, and an aluminium oxide third protective layer 107 of 45 nm in thickness.

<u>Examples 7-9</u>

A surface reflecting mirror 101 as shown in Fig. 2 was manufactured by forming the following layers on a polycarbonate resin substrate 102 of 2 mm in thickness by vacuum evaporation: a silicon dioxide under layer 103 having a thickness of 50 nm

(example 7), 200 nm (example 8) or 350 nm (example 9), an aluminum reflecting layer 104 of 100 nm in thickness, a silicon dioxide first protective layer 105 of 52 nm in thickness, a zirconium oxide second protective layer 106 of 40 nm in thickness, and an aluminum oxide third protective layer 107 of 45 nm in thickness.

Reference example 1

A surface reflecting mirror was manufactured by forming the following layers on a polycarbonate substrate of 2 mm in thickness by vacuum evaporation: an aluminum reflecting layer of 100 nm in thickness, a silicon dioxide first protective layer of 52 nm in thickness, a titanium oxide second protective layer of 33 nm in thickness, and an aluminum oxide third protective layer of 45 nm in thickness.

Reference example 2

A surface reflecting mirror 21 as shown in Fig. 1 was manufactured by forming the following layers on a polycarbonate substrate 22 of 2 mm in thickness by vacuum evaporation: a chromium oxide under layer 23 of 15 nm in thickness, an aluminum reflecting layer 24 of 100 nm in thickness, a silicon dioxide first protective layer 25 of 52 nm in thickness, a titanium oxide second protective layer 26 of 33 nm in thickness, and an aluminum oxide third protective layer 27 of 45 nm in thickness.

Reference examples 3-5

A surface reflecting mirror 41 as shown in Fig. 7 was manufactured by forming the following layers on a polycarbonate substrate 42 of 2 mm in thickness by vacuum evaporation: a silicon dioxide under layer 43 of 200 nm in thickness, an aluminum reflecting layer 44 of 100 nm in thickness, a silicon dioxide first protective layer 45 of 95 nm in thickness, and a 65-nm thick second protective layer 46 of titanium oxide (reference example 3), tantalum oxide (reference example 4) or zirconium oxide (reference example 5).

The samples of examples 1-9 and reference examples 1-5 were subjected to the following tests.

[Test for resistance to scratching]

The surface of a surface reflecting mirror sample was subjected to 20 times of go-and-return rubbing with a pressure of about 0.5 kg/cm^2 using lens-cleaning paper that had been immersed in a mixture solvent of ether and methanol, and was observed to find abnormalities such as a scratch.

[Test for film adhesiveness]

A cellophane tape was stuck to a surface reflecting mirror sample, and then removed therefrom strongly. The surface of the sample was observed to find abnormalities such as peeling.

[Test for resistance to humidification]

A surface reflecting mirror sample was placed in a thermostat at 60°C and 90% RH for 48 hours, and was observed to find abnormalities such as a crack and a point-like defect.

Results of the above tests were as shown in Table 1. Mark "O" in Table 1 indicates that no abnormality was found.

Table 1

	Test for resistance to scratching	Test for film adhesiveness	Test for resistance to humidification
Example 1	O	O	O
Example 2	O	O	O
Example 3	O	O	O
Example 4	O	O	O
Example 5	O	O	O
Example 6	O	O	O
Example 7	O	O	O
Example 8	O	O	O
Example 9	O	O	O
Reference example 1	O	peeling	point-like defects
Reference example 2	O	O	point-like defects
Reference example 3	large scratch	O	O
Reference example 4	large scratch	O	O
Reference example 5	large scratch	O	O

As described above, the surface reflecting mirror according to the embodiment is advantageous in the resistance to scratching because the third protective layer as the uppermost layer is made of aluminum oxide. In addition, by virtue of the under layer made of silicon dioxide, point-like defects can effectively be prevented from occurring between the

resin substrate and the film structure when the surface reflecting mirror is placed in a high temperature, high humidity atmosphere. Therefore, the surface reflecting mirror can be provided which can suitably be used for cameras, telescopes, microscopes, laser printers, bar code readers, etc.

CLAIMS

1. A surface reflecting mirror comprising:

a resin substrate;

an under layer made of silicon dioxide and formed on the resin substrate;

a reflecting layer made of aluminium and formed on the under layer;

a first protective layer made of silicon dioxide and formed on the reflecting layer;

a second protective layer made of at least one material selected from the group consisting of titanium oxide, tantalum oxide and zirconium oxide, and formed on the first protective layer; and

a third protective layer made of aluminum oxide and formed on the second protective layer.

2. A surface reflecting mirror as claimed in Claim 1, wherein a thickness of the under layer is within a range of 50-350 nm, a thickness of the reflecting layer is within a range of 50-250 nm, and thicknesses of the first to third protective layers are 42-133 nm, 24-89 nm and 10-110 nm, respectively.

3. A surface reflecting mirror substantially as hereinbefore described with reference to any one of Examples 1 to 9 and reference Examples 1 to 5 and the corresponding drawings.

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Examiner's report to the Comptroller under Section 17
(The Search report)

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Application number
GB 9421648.8

Relevant Technical Fields

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(ii) Int Cl (Ed.5) C23C

Databases (see below)
(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii)

Search Examiner
MR C ROSS

Date of completion of Search
15 NOVEMBER 1994

Documents considered relevant following a search in respect of Claims :-
1-3

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2241709 A (ASAHI)	1-3

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